US-PAT-NO: 4053537

DOCUMENT-IDENTIFIER: US 4053537 A

TITLE: Process for the production of elastic composites

---------- KWIC ---------

According to the invention, particularly preferred binders are mixtures of **prepolymers** containing free isocyanate groups and isocyanates free from urethane groups which have been obtained by reacting **polyisocyanates with polyhydroxy polyethers in an NCO:OH ratio** of 2:1 to 15:1. Such polyisocyanate binders should best have a viscosity in the range from 500 to 20,000 mPas, preferably in the range from 1,000 to 10,000 mPas, at 20.degree. C. The binders are generally hardened by reaction with water, usually in the form of atmospheric moisture, in which case there is an additional reaction between the binder and the paste described in the following.

2. The process of claim 1, wherein the polyisocyanate binder is a mixture of **prepolymers** containing isocyanate groups and isocyanates free from urethane groups, said mixture obtained by reacting **polyisocyanates with polyhydroxy polyether in a NCO to OH ratio** of from 2:1 to 15:1.

US-PAT-NO: 4025579

DOCUMENT-IDENTIFIER: US 4025579 A

TITLE: Process for the production of sheet-like structures

---------- KWIC ---------

The binders used in the process according to the invention are **prepolymers** which contain free isocyanate groups mixed with isocyanates which are free from urethane groups, the said mixtures having been obtained by reacting **polyisocyanates with polyhydroxyl polyethers at an NCO/OH ratio** of from about 2:1 to 15:1 preferably from about 4:1 to 10:1.

US-PAT-NO: 4126428

DOCUMENT-IDENTIFIER: US 4126428 A

TITLE: Coated abrasive containing isocyanurate binder and method of producing same

---------- KWIC ---------

Where the isocyanate-terminated **urethane prepolymer** is made from **polyisocyanate-polyol reaction mixtures, the mixtures can have NCO/OH equivalent ratios** greater than 1, preferably at least 1.2/1 to 6/1. Generally, the greater the amount of isocyanurate in the resulting product the greater its hardness. The preferred products are those which are highly crosslinked by reason of having about 20% to 85% of the isocyanate groups in the reaction mixture converted to isocyanurate linkages or when moisture is present during polymermization, also urea linkages.

Two parts of the isocyanate-lactate catalyst concentrate was diluted with 8 parts of an isocyanate-terminated **prepolymer** made by reacting 75 parts of "Mondur" MRS with 25 parts of a 1500 molecular weight triol, having an equivalent weight of 500 and being prepared from trimethylol propane, propylene oxide and potassium hydroxide, to obtain a coating mixture hereinafter identified as mixture "A," having approximately an 80:20 **isocyanate polyol ratio**. A thin film of mixture "A" was cured by placing in an oven at 90.degree. C. for 2 minutes. The cured polyisocyanurate resin obtained had an average Knoop hardness number of 21.

US-PAT-NO: 4798878

DOCUMENT-IDENTIFIER: US 4798878 A

TITLE: Synthetic resin compositions shelf-stable under exclusion of moisture

---------- KWIC ---------

The above-mentioned polymerization and polycondensation products are conventionally converted with di- and/or polyisocyanates into so-called isocyanate **prepolymers** which contain isocyanate groups. If a chain-lengthening reaction by way of urethane groups (OH+N.dbd.C.dbd.O) can be tolerated or is even desirable, then the hydroxy-group-containing polymerization or polycondensation products are reacted in an NCO OH ratio of about 1.1-2.5:1 with the di- or poly-isocyanates. By "poly" here is meant generally up to 5 preferably 3 isocyanate groups in a compound or polyisocyanates of up to about 50 monomer units (**prepolymers**). If a chain-extending reaction is undesirable, then a substantially larger excess of di- or **polyisocyanate is utilized, calculated preferably for an NCO/OH ratio** of about 3-5; otherwise, the reaction is carried out in the same way as in the case of the lower NCO/OH ratios, see, e.g., U.S. Pat. No. 3,941,753 column 3 lines 20-42. which disclosure is incorporated by reference herein. The excess di- or polyisocyanate is removed, for example in case of distillable di- or polyisocyanates by thin-film distillation or, in case of isocyanates that cannot be distilled, by means of solvent extraction.

US-PAT-NO: 5116932

DOCUMENT-IDENTIFIER: US 5116932 A

TITLE: Hydrolysis resistant polyurethane resins

---------- KWIC ---------

The preparation of polyurethanes according to the present invention can be accomplished either by the **prepolymer** process in which a polyol and an excess of an organic diisocyanate compound are allowed to react to form a **prepolymer** having isocyanate group in terminal positions and the **prepolymer** is allowed to react with a diol, diamine, etc., as a chain extender, or by a one-shot process in which all of the constituents required for making a polyurethane are added simultaneously. The **ratio of polyol and chain extender to diisocyanate** may vary over a wide range. Preferably the NCO/OH is about 0.5 to 3.0 equivalently, more preferably 0.07 to 1.1.

US-PAT-NO: 4882112

DOCUMENT-IDENTIFIER: US 4882112 A

TITLE: Process for producing shaped articles from vegetable particulate materials

---------- KWIC ---------

The **urethane prepolymer** terminated with free isocyanato groups may be prepared by reacting the **polyisocyanate compound and the polyether polyol at an NCO/OH equivalent ratio** of 1.5 to 100, preferably 2 to 20. The resulting **prepolymer** may be easily dissolved or dispersed in a large excess of water optionally together with a binder polymer to form a binder liquid for bonding vegetable particulate materials. Water acts as a chain extender of the **urethane prepolymer**.

US-PAT-NO: 5134216

DOCUMENT-IDENTIFIER: US 5134216 A

TITLE: Epoxide-containing two-component polyurethane adhesives

---------- KWIC ---------

Suitable higher molecular weight polyisocyanates are modification products of such polyisocyanates, i.e. polyisocyanates having e.g. isocyanurate, carbodiimide, allophanate, biuret or uretdione structural units, such as can be prepared from the polyisocyanates of the type mentioned by processes of the prior art which are known per se. Of the higher molecular weight modified polyisocyanates, the **prepolymers** known from polyurethane chemistry having terminal isocyanate groups and of the molecular weight range from 400 to 10,000 preferably from 600 to 8,000 and in particular from 800 to 5,000, are of particular interest. These compounds are prepared in a manner which is known per se by reaction of excess amounts of polyisocyanates with organic compounds having at least two groups which are reactive towards isocyanate groups, in particular organic polyhydroxy compounds. Suitable such polyhydroxy compounds are both simple polyhydric alcohols of the molecular weight range from 62 to 599, preferably from 62 to 200, such as e.g. ethylene glycol, trimethylolpropane, propane-1,2-diol or butane-1,2-diol, and higher molecular weight polyether-polyols and/or polyester-polyols of the type generally known from polyurethane chemistry and having molecular weights from 600 to 8,000, preferably from 800 to 4,000, which contain at least two, as a rule 2 to 8, but preferably 2 to 4, primary and/or secondary hydroxyl groups. It is of course also possible to use those NCO **prepolymers** which have been obtained from polyisocyanates and less preferred compounds having groups which are reactive towards isocyanate groups, such as e.g. polythioether-polyols, polyacetals containing hydroxyl groups, polyhydroxy-polycarbonates, polyester-amides containing hydroxyl groups or copolymers, containing hydroxyl groups, of olefinically unsaturated compounds. Compounds which have groups which are reactive towards isocyanate groups, in particular hydroxyl groups, and are suitable for the preparation of the NCO **prepolymers** are, for example, the compounds disclosed as examples in U.S. Pat. No. 4,218,543, column 7, line 29, to column 9, line 25. In the preparation of the NCO **prepolymers,** these compounds have groups which are reactive towards **isocyanate groups are reacted with polyisocyanates at an NCO/OH equivalent ratio** of about 1.5:1 to 20:1,

preferably 5:1 to 15:1. The NCO **prepolymers** in general have an NCO content of 2.5 to 25, preferably 7 to 22 wt. %. From this, it can already be seen that in the context of the present invention, by "NCO **prepolymers" and by "prepolymers** having terminal isocyanate groups" there are to be understood both the reaction products as such and their mixtures with excess amounts of unreacted starting polyisocyanates, which are often also called "semi-prepolymers".

US-PAT-NO: 5227451

DOCUMENT-IDENTIFIER: US 5227451 A

TITLE: Urethane prepolymer and polyurethane compositions comprising the prepolymer

---------- KWIC ---------

This object is attained by a **urethane prepolymer** containing isocyanate groups which is obtained by reacting erythritol with 2 to 8 mols of an alkylene oxide or lactone per mol of erythritol to prepare a polyol containing four functional groups, and by reacting the **polyol with a di-isocyanate in a reaction equivalent ratio** (isocyanate groups/hydroxyl groups) of 3-20, and by a polyurethane composition which is prepared from any such **prepolymer** and a polyol.

The **urethane prepolymer of this invention is a prepolymer** containing isocyanate groups and obtained by reacting erythritol with 2 to 8 mols of an alkylene oxide or lactone per mol of erythritol to prepare a polyol containing four functional groups, and by reacting the **polyol with a di-isocyanate in a reaction equivalent ratio** (isocyanate groups/hydroxyl groups) of 3-20.

An average of 2 to 8 mols of alkylene oxide is preferably reacted with 1 mol of erythritol. The use of the alkylene oxide in a **proportion below 2 mols gives a polyol having low compatibility with the di-isocyanate,** and results in failure to produce a uniform **urethane prepolymer**. The use of alkylene oxide in a proportion above 8 mols is also undesirable, as it results in the formation of a **urethane prepolymer** having too low an isocyanate content.

An average of 2 to 8 mols of lactone is preferably reacted with 1 mol of erythritol. The use of the lactone in a **proportion below 2 mols gives a polyol having low compatibility with the di-isocyanate,** and results in failure to produce a uniform **urethane prepolymer**. The use of the lactone in any proportion above 8 mols is also undesirable, as it results in the formation of a **urethane prepolymer** having too low an isocyanate content.

The reaction between the **polyol and the diisocyanate is preferably carried out in a mixture thereof having an equivalent ratio** of isocyanate/hydroxyl

groups ranging between 3 and 20. If the ratio is below 3 the reaction is likely to yield a **urethane prepolymer** having a high molecular weight, or even a gelated product. If the ratio is over 20 a large amount of diisocyanate remains unreacted and its removal is very difficult.

The polyurethane composition of this invention comprises a mixture of **urethane prepolymer and polyol giving an equivalent ratio of isocyanate**/hydroxyl groups (which may hereinafter be stated as (NCO/OH)) ranging between 0.5 and 2.0. If the ratio is below 0.5 the composition fails to be satisfactorily crosslinked and yields a hardened product which is low in hardness, and chemical and solvent resistance. If the ratio is over 2.0, the composition yields a hardened product which is brittle and of low impact resistance.

In each example, the urethane **prepolymer and the polyol were mixed in proportions making a mixture having an NCO**/OH value (equivalent ratio) of 1.

1. A **urethane prepolymer** containing isocyanate groups which is obtained by reacting erythritol with 2 to 8 mols of an alkylene oxide or lactone per mol of erythritol to form a polyol containing four functional groups, and reacting said **polyol and a di-isocyanate in a mixture giving an equivalent ratio** of isocyanate to hydroxyl groups ranging between 3 to 20.

US-PAT-NO: 5290853

DOCUMENT-IDENTIFIER: US 5290853 A
See image for Certificate of Correction

TITLE: Ambient moisture-curing polyurethane adhesive

---------- KWIC ---------

In accordance with the invention, a one-part, ambient moisture-curable polyurethane adhesive which is dispensed for use from a substantially hermetically sealed container is produced by reacting about 30 to about 50 weight % of a polyol selected from the group consisting of polyether diols, triols and tetrols based on propylene glycol or ethylene oxide-capped propylene glycol and mixtures thereof and having an average molecular weight of about 1000 to about 10,000 with an organic polyisocyanate having a functionality greater than 2, at a **ratio of isocyanate equivalents to polyol** equivalents of about 3:1 to about 15:1, for a sufficient time to form a polyurethane reaction product including an isocyanate-terminated **prepolymer** and unreacted isocyanate (polyol-isocyanate reaction); admixing with the resulting reaction product at least one additive selected from the group consisting of thixotropic agents, fillers, antioxidants, plasticizers, solvents, pigments, adhesive promoters, UV stabilizers and defoaming agents containing a sufficient total amount of free water to provide a ratio of water equivalents to polyol equivalents of about 0.2:1 to about 2:1, whereby the free water reacts with unreacted isocyanate in the reaction product to extend the molecular chain of said polyurethane and provide hard segments therein (water-isocyanate reaction); allowing the water-isocyanate reaction to proceed until a predetermined amount of unreacted isocyanate remains to produce an isocyanate-terminated polymer adhesive containing unreacted isocyanate; and introducing the resulting adhesive into a substantially hermetically sealed container.

The polyol is reacted with an excess of polyisocyanate so that a reaction product containing an isocyanate-terminated **polyurethane prepolymer** and unreacted isocyanate is produced. The amount of polyisocyanate used is sufficient to provide a **ratio of isocyanate equivalence to polyol** equivalence of about 3:1 to about 15:1, preferably about 5:1 to about 10:1. The particular ratio used depends primarily on the desired flexibility characteristics of the adhesive, with flexibility decreasing as this ratio increases. It has been

found that, when a polymeric MDI having a functionality of about 2.2-2.5 and a free isocyanate value of 31-32% is used with a diol having an average molecular weight of about 4000 or a triol having an average molecular weight of about 6000, a **ratio of isocyanate equivalents to polyol** equivalents of about 8:1 produces an adhesive exhibiting good tensile strength, while maintaining excellent adhesive properties.

reacting about 30 to about 50 weight %, based on the total weight of the adhesive, of a polyol selected from the group consisting of polyether diols, triols and tetrols based on propylene glycol or ethylene oxide-capped propylene glycol and mixtures thereof and having an average molecular weight of about 1000 to about 10,000, with an organic polyisocyanate having a functionality greater than 2, at a **ratio of isocyanates equivalents to polyol** equivalents of about 3:1 to about 15:1, for a sufficient time to form a polyurethane reaction product including an isocyanate-terminated **prepolymer** and unreacted isocyanate (polyol-isocyanate reaction);

reacting about 30 to about 50 weight %, based on the total weight of the adhesive, of a polyol selected from the group consisting of polyether diols based on propylene glycol or ethylene oxide-capped propylene glycol having a molecular weight of about 2000 to about 6000, triols based on propylene glycol or ethylene-capped propylene glycol having a molecular weight of about 2500 and about 8500 and mixtures thereof and with an organic polyisocyanate having a functionality greater than 2, at a **ratio of isocyanates equivalents to polyol** equivalents of about 5:1 to about 10:1, for a sufficient time to form a polyurethane reaction product including an isocyanate-terminated **prepolymer** and unreacted isocyanate (polyol-isocyanate reaction);

US-PAT-NO: 5486547

DOCUMENT-IDENTIFIER: US 5486547 A

TITLE: Surgical adhesive sheet, surgical instruments and methods of using the same

---------- KWIC ---------

In reacting at least one polyisocyanate (a) with at least one hydrophilic polyether polyol (b) and optionally one or more other **polyols (c) to form NCO-terminated hydrophlic urethane prepolymers, ratio** of NCO/OH is usually 1.5-5.0, preferably 1.7-3.0. The reaction of (a) with (b) and optionally (c) forming **prepolymers** can be performed in the usual manner. The reaction may be carried out in the presence of a catalyst. **Prepolymers** may be prepared by reacting (a) with a mixture of (b) and (c), or reacting successively in any order with (b) and (c). **Prepolymers** may be prepared by blending a **prepolymer** from (b) with a **prepolymer** from (c) (for instance, blending with a **prepolymer** from a low molecular weight polyol (equivalent weight 50-500) to reduce viscosity).

US-PAT-NO: 5508111

DOCUMENT-IDENTIFIER: US 5508111 A
See image for Certificate of Correction

TITLE: Adhesive composition

---------- KWIC ---------

27. In an adhesive composition comprising a resin system, a catalyst, optionally one or more fillers and optionally a pigment and/or dye, and wherein said resin system comprises a **prepolymer** and a curative composition, said **prepolymer being a urethane prepolymer** formed by reacting a **polyol with polyisocyanate in a equivalent ratio (NCO**/OH) of about 2 to about 20 and said curative composition comprising a primary polyamine and a polyol and wherein the isocyanate index NCO/(OH+NH.sub.2) of said resin system is about 1.20 to 2, the improvement wherein said composition is free of fast reacting primary aliphatic amines and wherein said polyamine of said curative is one or more primary aromatic polyamines with fused polycyclic aromatic rings having at least 2 NH.sub.2 groups per molecule, and having H, NH.sub.2, C.sub.1 to C.sub.5 alkyl, or phenyl groups attached to the ring carbons which are not bridge-head carbons.

US-PAT-NO: 5880167

DOCUMENT-IDENTIFIER: US 5880167 A

TITLE: Polyurethane compositions with a low content of monomeric diisocyanates

---------- KWIC ---------

According to the Schulz-Flory statistic, the content of monomeric diisocyanate in the reaction product where diisocyanates containing isocyanate groups of equal reactivity are used is dependent on the NCO:OH ratio used in the synthesis of the **prepolymer**: ##EQU1## where .beta. is the content of monomeric **diisocyanate and a is the NCO:OH ratio** (see, for example, R. Bonart, P. Demmer, GPC-Analyse des Gehaltes an monomerem Diisocyanat in Prepolymeren von segmentierten Polyurethanen (GPC Analysis of the Content of Monomeric Diisocyanate in **Prepolymers** of Segmented Polyurethanes, Colloid and Polymer Sci., 260 518-523 (1982)). With an NCO:OH ratio of 2, as frequently necessary for the composition of the **prepolymer,** 25% of the diisocyanate used remain as monomer in the **prepolymer**. If, for example, 10% by weight of diphenyl methane **diisocyanate (MDI) are used for synthesis of the prepolymer at an NCO:OH ratio** of 2, approximately 2% by weight of monomeric MDI is found in the **prepolymer** in accordance with the above statistical estimation. At an application temperature of 150.degree. C., the MDI already has a vapor pressure of around 0.8 mbar. Under the application conditions described above, particularly if the composition is applied in thin layers as an adhesive over large surface areas, considerable quantities of this residual monomer enter the overlying air space and have to be removed by extraction.

There are no critical aspects to the composition of the NCO **prepolymers** for the foamable compositions. This is because, according to the prior art, the **prepolymer** is almost always directly produced in the pressurized containers from mixtures of technical diphenyl methane-4,4'**-diisocyanate (MDI) with a functionality of 2.3 to 2.7 and polyols with an NCO:OH ratio** of 3-10 and preferably 4-6:1 in the presence of a tertiary amine as catalyst. On account of the excess of MDI, free unreacted MDI is still present in large quantities of the order of 7 to 15% by weight, based on the total content of the pressurized container. On account of this content of monomeric MDI, the compositions have to be labeled as harmful by inhalation, "harmful to health",

"contains diphenyl methane-4,4'-diisocyanate" and with the "St. Andrews cross" danger symbol. If more readily volatile polyisocyanates were to be used instead of MDI for the production of the **prepolymer,** the reaction mixtures would likewise contain relatively large quantities of unreacted diisocyanate. Under the law on hazardous materials, these products would even have to be labeled as "toxic" and with the "death's head" danger symbol. On account of this increased toxicity, readily volatile diisocyanates have not been used in insulation and assembly foams from aerosol cans. In addition, the cure times of **prepolymers** of aliphatic or cycloaliphatic diisocyanates are too short for use as one-component insulation and assembly foams. Accordingly, only MDI is actually used for this purpose.

US-PAT-NO: 6072019

DOCUMENT-IDENTIFIER: US 6072019 A

TITLE: Water-based polyurethane polymer, release coating, adhesive tape and process of preparation

---------- KWIC ---------

The **ratio of isocyanate groups to the total available isocyanate-reactive hydroxyl groups (NCO**:OH) in the first reaction stage is preferably close to the theoretical ratio of 2:1 to form a diisocyanate **prepolymer,** for example from 1.8 to 2:1, or even 1.95:1, but can range from as low as 1.4:1 to as high as 5:1.

US-PAT-NO: 6462163

DOCUMENT-IDENTIFIER: US 6462163 B2

TITLE: Solventless laminating adhesive with barrier properties

---------- KWIC ---------

It is within the scope of the invention, and is in some cases preferred, that a portion A') of the polyester A) be reacted with all of or a portion B') of the **isocyanate B) at an NCO/OH ratio** of between about 2 and about 8 to form a **urethane prepolymer** C), and the remaining portion A") of the polyester A) subsequently admixed with the **prepolymer** C) and any remaining portion B") of the isocyanate B) to form an adhesive mixture suitable for laminating the adhesives. In such case, the NCO/OH ratio of B), including in such case B') and B"), to A), including both A') and A"), is, nevertheless, between about 1 and about 1.1.

US-PAT-NO: 6303731

DOCUMENT-IDENTIFIER: US 6303731 B1

TITLE: Moisture curable polyurethane compositions

---------- KWIC ---------

The polyisocyanate preferably has at least 2.0 isocyanate groups but may have less than 2 isocyanate groups. The **polyisocyanate and the polyol are selected to produce a reaction mixture having a NCO:OH ratio** of from about 1.5 to about 4.0, preferably from about 1.5 to about 3.0, more preferably from about 2.0 to about 3.0. One of skill in the art would understand how to achieve the desired NCO:OH ratio. The % residual NCO present after the **prepolymer** is made but prior to cure is preferably less than about 1.5%, more preferably less than about 1.0%.

The **polyurethane prepolymer** phase is typically prepared by reacting the polyol or polyols with at least one polyfunctional isocyanate compound at an elevated temperature of typically between about 40.degree. C. and about 120.degree. C., and more preferably between about 60.degree. C. and about 90.degree. C. The polyols may first be introduced into a reaction vessel, heated to reaction temperatures and dried to remove ambient moisture absorbed by the polyols. The polyfunctional isocyanate is then added to the reactor. The **polyols are generally reacted with the isocyanate compounds at ratios** that typically depend on the hydroxy and isocyanate functionality of the reactants. Typically the compounds are reacted at ratios that result in a reaction between isocyanate groups and hydroxy groups leaving essentially no residual hydroxy and minimal isocyanate functionality. The reaction between the **polyol compounds and the isocyanate compounds is conducted at an NCO:OH ratio** of from
about 1.5:1.0 to about 4.0:1.0 in order to obtain an NCO concentration in the final composition, prior to cure, of from about 0.1% by weight to about 3.0% by weight, preferably less than about 1.5% by weight, more preferably less than about 1.0% by weight. Typically, the **prepolymer** is titrated to measure residual concentration of isocyanate using ASTM D-2572-80 "Standard Method for Isocyanate Group and Urethane Materials or **Prepolymers**" to determine completion of the reaction. If the NCO:OH ratio is higher, the storage modulus, G', increases and the **prepolymer** may become too stiff as a result making the

composition either less pressure sensitive or even non-pressure sensitive. In other words, the tack and pressure sensitivity may decrease resulting in a composition that is not suitable as a pressure sensitive adhesive or coating.

DOCUMENT-IDENTIFIER: US 20010013393 A1

TITLE: Solventless laminating adhesive with barrier properties

---------- KWIC ---------

[0008] It is within the scope of the invention, and is in some cases preferred, that a portion A') of the polyester A) be reacted with all of or a portion B') of the **isocyanate B) at an NCO/OH ratio** of between about 2 and about 8 to form a **urethane prepolymer** C), and the remaining portion A") of the polyester A) subsequently admixed with the **prepolymer** C) and any remaining portion B") of the isocyanate B) to form an adhesive mixture suitable for laminating the adhesives. In such case, the NCO/OH ratio of B), including in such case B') and B"), to A), including both A') and A"), is, nevertheless, between about 1 and about 1.1.

[0021] An NCO/OH ratio of 1 is theoretically desired in reacting the polyester with the isocyanate, whether the polyester is reacted with a diisocyanate or whether a **urethane prepolymer** is reacted with a polyester. However, as the polyester may contain some residual water from the polyester condensation reaction, a slight excess of **diisocyanate is typically used, up to an NCO/OH ratio** of about 1.1.

1. A method of laminating a first film of polymeric material to a second film of polymeric material comprising: (a) providing, in molten form, a solventless, hydroxyl-terminated polyester A) formed from a single species of a linear aliphatic diol having terminal hydroxyl groups and having from 2 to 10 carbons and a single species of a linear dicarboxylic acid, said polyester having a number average molecular weight from about 300 to about 5000 and a melting point of 80.degree. C. or below, (b) providing, in liquid form, a single species of diisocyanate B), either (c) mixing said **diisocyanate B) and said polyester A) at an NCO/OH ratio** of between about 1 and 1.1 to form an adhesive mixture (I), or reacting all of or a portion B') of said diisocyanate B) with a portion A') of said polyester A) at an NCO/OH ratio of between about 2 and 8 to form a **urethane prepolymer** C) and mixing the remaining portion A") of said polyester A) and any remaining portion B") of said diisocyanate B) with said **urethane prepolymer** C) to form an adhesive mixture (II), the NCO/OH ratio of A) to B) being between about 1 and 1.1, (d) applying either of the adhesive mixture (I) or (II) to one of said first or second films, said adhesive mixture

being prepared just prior to application to said film, (e) contacting and adhering said films such that crystalline polyester domains are formed prior to substantial cure of said mixture and attendant polyurethane adhesive formation, and (f) allowing said diisocyanate B) and said polyester A) to fully react, thereby forming an adhesive layer having high gas barrier properties.

US-PAT-NO: 5880167

DOCUMENT-IDENTIFIER: US 5880167 A

TITLE: Polyurethane compositions with a low content of monomeric diisocyanates

---------- KWIC ---------

According to the Schulz-Flory statistic, the content of monomeric diisocyanate in the reaction product where diisocyanates containing isocyanate groups of equal reactivity are used is dependent on the NCO:OH ratio used in the synthesis of the prepolymer: ##EQU1## where .beta. is the content of monomeric **diisocyanate and a is the NCO:OH ratio** (see, for example, R. Bonart, P. Demmer, GPC-Analyse des Gehaltes an monomerem Diisocyanat in Prepolymeren von segmentierten Polyurethanen (GPC Analysis of the Content of Monomeric Diisocyanate in Prepolymers of Segmented Polyurethanes, Colloid and Polymer Sci., 260 518-523 (1982)). With an NCO:OH ratio of 2, as frequently necessary for the composition of the prepolymer, 25% of the diisocyanate used remain as monomer in the prepolymer. If, for example, 10% by weight of diphenyl methane **diisocyanate (MDI) are used for synthesis of the prepolymer at an NCO:OH ratio** of 2, approximately 2% by weight of monomeric MDI is found in the prepolymer in accordance with the above statistical estimation. At an application temperature of 150.degree. C., the MDI already has a vapor pressure of around 0.8 mbar. Under the application conditions described above, particularly if the composition is applied in thin layers as an adhesive over large surface areas, considerable quantities of this residual monomer enter the overlying air space and have to be removed by extraction.

There are no critical aspects to the composition of the NCO prepolymers for the foamable compositions. This is because, according to the prior art, the prepolymer is almost always directly produced in the pressurized containers from mixtures of technical diphenyl methane-4,4'**-diisocyanate (MDI) with a functionality of 2.3 to 2.7 and polyols with an NCO:OH ratio** of 3-10 and preferably 4-6:1 in the presence of a tertiary amine as catalyst. On account of the excess of MDI, free unreacted MDI is still present in large quantities of the order of 7 to 15% by weight, based on the total content of the pressurized container. On account of this content of monomeric MDI, the compositions have to be labeled as harmful by inhalation, "harmful to health",

"contains diphenyl methane-4,4'-diisocyanate" and with the "St. Andrews cross" danger symbol. If more readily volatile polyisocyanates were to be used instead of MDI for the production of the prepolymer, the reaction mixtures would likewise contain relatively large quantities of unreacted diisocyanate. Under the law on hazardous materials, these products would even have to be labeled as "toxic" and with the "death's head" danger symbol. On account of this increased toxicity, readily volatile diisocyanates have not been used in insulation and assembly foams from aerosol cans. In addition, the cure times of prepolymers of aliphatic or cycloaliphatic diisocyanates are too short for use as one-component insulation and assembly foams. Accordingly, only MDI is actually used for this purpose.

A hotmelt adhesive was produced by a single-stage process as in Example 2 from 133.4 parts of Dynacoll 7360, 66.6 parts of Dynacoll 7250, 14.4 parts of benzyl alcohol and 47.9 parts of triphenyl methane-4,4',4"-triisocyanate. The functionality of the isocyanate is reduced from f=3.0 to f=1.89 by addition of the benzyl alcohol as terminator. The **NCO:OH ratio, based on polyol and isocyanate,** is 2,28/1.0.

The chain terminator 1-hexanol used in this Example reduces the functionality of the isocyanate used to 2.0 (calculated). The effective **NCO:OH ratio is 2.0, based on the polyol** OH groups.

US-PAT-NO: 6111048

DOCUMENT-IDENTIFIER: US 6111048 A

TITLE: Blocked polyisocyanate and uses thereof

---------- KWIC ---------

In the coating composition of the present invention, the equivalent **ratio of the blocked isocyanate groups in the blocked polyisocyanate to the hydroxyl groups in the polyol** is selected in accordance with the desired properties of the coating, but is usually in the range of from 10:1 to 1:10.

The epoxy polyol prepared in Reference Example 8 and the blocked polyisocyanate prepared in Example 1 were mixed with each other so that the equivalent **ratio of the blocked isocyanate groups/hydroxyl groups of the epoxy polyol** became 1:2, to obtain a mixture. To the mixture was added 0.5% by weight of dibutyltin dilaurate, based on the total weight of the solids in the mixture of the blocked polyisocyanate and epoxy polyol. The resultant mixture was diluted with methyl isobutyl ketone, so that the content of the solids became 25% by weight, to thereby obtain a coating composition. For evaluating the coating composition, the coating composition was coated onto a tin plate (size: 50 mm.times.150 mm) using an applicator, and dried at room temperature for 30 minutes to thereby obtain a coating. The obtained coating was baked at 120.degree. C. for 30 minutes in an oven. With respect to the baked coating, the gel ratio was measured by the above-mentioned method. Results are shown in Table 3.

US-PAT-NO: 6218471

DOCUMENT-IDENTIFIER: US 6218471 B1

TITLE: Adhesive compositions based on ethylene-unsaturated acid ester copolymers and containing hydroxyl functional groups

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(ii) addition and reaction of an alcohol and of the **polyisocyanate until the required proportion of NCO** is obtained.

The excess needed depends on the OH content of the copolymer (A) and on the diisocyanate employed (a diisocyanate in which both NCO functional groups have the same reactivity (MDI) requires a larger molar excess than a diisocyanate in which the two NCO functional groups do not have the same reactivity (TDI)). With a proportion of approximately 2% of hydroxyl monomer, the operation is carried out, for example in the case of **MDI, with a total NCO/copolymer (A) OH ratio** of approximately 15 to 25. The excess diisocyanate is next neutralized by addition of a single monoalcohol (lauryl alcohol, stearyl alcohol) or of a monoalcohol-dialcohol mixture, such that the final total NCO/total OH ratio is between 1.5 and 2.5 and preferably 1.8 to 2.2.

(ii) addition and reaction of an alcohol and of the **polyisocyanate until the required proportion of NCO** is obtained.

US-PAT-NO: 6376602

DOCUMENT-IDENTIFIER: US 6376602 B1

TITLE: Coating compositions, a process for their production and their use for coating water-resistant substrates

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The present invention also relates to a process for the production of these coating compositions by emulsifying the polyisocyanate component in an aqueous or aqueous/organic dispersion of the **polyol component in amounts corresponding to an equivalent ratio of isocyanate** groups to alcoholic hydroxyl groups of 0.2:1 to 5:1 and, prior to the addition of the polyisocyanate, incorporating any auxiliaries and additives into the polyol component.

The quantity in which the **polyisocyanate component is used is selected to provide an NCO:OH equivalent ratio,** based on the isocyanate groups of component b) and the alcoholic hydroxyl groups of component a), including the hydroxyl groups of any water-soluble, low molecular weight polyhydroxyl compounds used, of 0.2:1 to 5:1, preferably 0.5:1 to 2:1. Before the addition of polyisocyanate component b), the known auxiliaries and additives used in coatings technology may be incorporated in polyol component a). The auxiliaries and additives include foam inhibitors, flow control agents, thickeners, pigments, dispersion aids for the dispersion of pigments, etc.

US-PAT-NO: 6417261

DOCUMENT-IDENTIFIER: US 6417261 B1

TITLE: Soap gel based glue stick

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5. The adhesive stick of claim 1 wherein said polyurethane is in the form of an aqueous dispersion and is a reaction product of (a) a mixture of such polyols (b) a component capable of salt formation in an alkaline aqueous solution and (c) a **polyisocyanate in an OH:NCO ratio** of 1.00:8 to 1.0.4.0.

US-PAT-NO: 6303731

DOCUMENT-IDENTIFIER: US 6303731 B1

TITLE: Moisture curable polyurethane compositions

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The polyisocyanate preferably has at least 2.0 isocyanate groups but may have less than 2 isocyanate groups. The **polyisocyanate and the polyol are selected to produce a reaction mixture having a NCO:OH ratio** of from about 1.5 to about 4.0, preferably from about 1.5 to about 3.0, more preferably from about 2.0 to about 3.0. One of skill in the art would understand how to achieve the desired NCO:OH ratio. The % residual NCO present after the prepolymer is made but prior to cure is preferably less than about 1.5%, more preferably less than about 1.0%.

The polyurethane prepolymer phase is typically prepared by reacting the polyol or polyols with at least one polyfunctional isocyanate compound at an elevated temperature of typically between about 40.degree. C. and about 120.degree. C., and more preferably between about 60.degree. C. and about 90.degree. C. The polyols may first be introduced into a reaction vessel, heated to reaction temperatures and dried to remove ambient moisture absorbed by the polyols. The polyfunctional isocyanate is then added to the reactor. The **polyols are generally reacted with the isocyanate compounds at ratios** that typically depend on the hydroxy and isocyanate functionality of the reactants. Typically the compounds are reacted at ratios that result in a reaction between isocyanate groups and hydroxy groups leaving essentially no residual hydroxy and minimal isocyanate functionality. The reaction between the **polyol compounds and the isocyanate compounds is conducted at an NCO:OH ratio** of from
about 1.5:1.0 to about 4.0:1.0 in order to obtain an NCO concentration in the final composition, prior to cure, of from about 0.1% by weight to about 3.0% by weight, preferably less than about 1.5% by weight, more preferably less than about 1.0% by weight. Typically, the prepolymer is titrated to measure residual concentration of isocyanate using ASTM D-2572-80 "Standard Method for Isocyanate Group and Urethane Materials or Prepolymers" to determine completion of the reaction. If the NCO:OH ratio is higher, the storage modulus, G', increases and the prepolymer may become too stiff as a result making the

composition either less pressure sensitive or even non-pressure sensitive. In other words, the tack and pressure sensitivity may decrease resulting in a composition that is not suitable as a pressure sensitive adhesive or coating.